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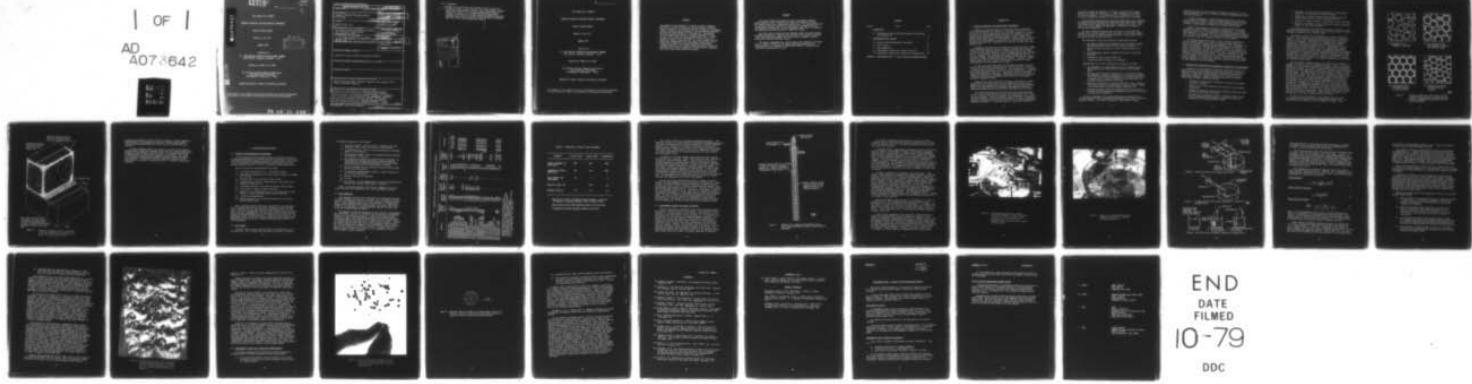
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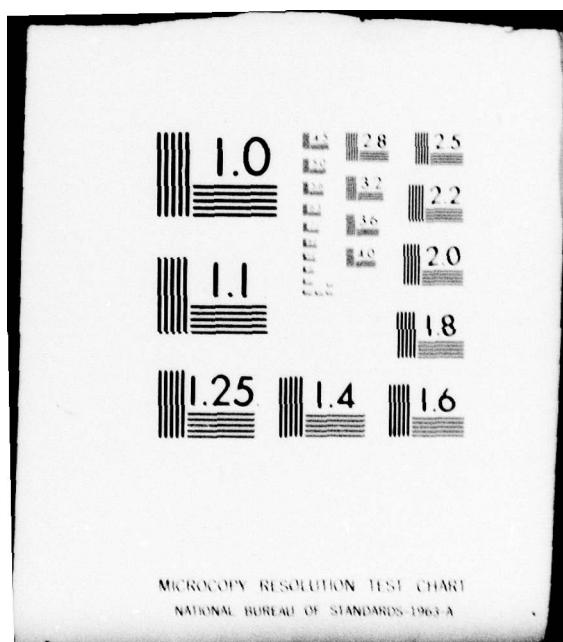
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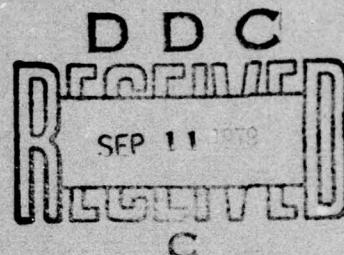
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COMPOSITE MATERIALS FOR MAXILLOFACIAL PROSTHESES

Annual Progress Report

Robert A. Erb, Ph.D.

AUGUST 1978



Supported by

U.S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
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ABSTRACT

The purpose of this program is to develop ultrasoft composite materials to be used as fillers in the fabrication of maxillo-facial prostheses. The projected composite systems are elastomeric-shelled, liquid-filled microcapsules. Two experimental approaches were pursued toward making such microcapsules. One approach involves coaxial extrusion of a catalyzed elastomer precursor and core liquid into a rotating, graded-density bath. A major problem to be solved with this approach is how to break the stream into small, closed capsules. The other approach involves interfacial polymerization of polyurethane around droplets of polyglycols formed in a continuum containing diisocyanate. Problems encountered here include keeping the spheres separately suspended until curing is complete, and producing an elastomeric shell only rather than forming solid beads.

FOREWARD

The concept behind this program is that a multiphase composite system should be able to simulate the mechanical properties of human soft tissue better than a homogeneous system could. The proposed composite of particular interest consists of liquid-filled, elastomeric-shelled microcapsules held together to form a deformable mass; this is to simulate the semi-liquid cellular structure of human soft tissue.

The first year's program has been directed toward the goal of making suitable microcapsules. Progress has been made in the areas of materials choice and process development, but further work is needed to provide satisfactory products with good yields.

The author acknowledges the contributions of Mr. Richard H. Hollinger and Mr. Joseph F. Heffron in the coaxial extrusion studies and the contributions of Dr. Stephen W. Osborn and Mr. Robert A. Henning in the interfacial polymerization studies.

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1. INTRODUCTION

1.1 History of materials for maxillofacial prosthetics

Clarke [1] at the beginning of his detailed book on prosthetics quotes Sushruta Samhita (ca. 600 B.C.) as follows: "The love of life is next to our love of our own face and thus the mutilated cry for help." Maxillofacial disfigurements beyond the scope of restorative surgery arise from any sources, including war wounds, accident trauma, birth defects, and radical surgery for malignancies. Maxillofacial prostheses, the artificial replacement of parts of the face and jaw, can help the disfigured person to be a functional part of social, economic and other areas of life.

Prosthetics and materials have always been closely related. Among natural materials used for facial prostheses, leather, wood, and metal could not produce lifelike parts not only because they are too rigid, but also for the basic reason that they are opaque whereas skin is translucent. Ordinary paint coatings, being opaque themselves, will not solve the problem. Wax and glass had translucency but were not durable and were too rigid to simulate facial soft tissue. Vulcanite, a hard-rubber composition used by dental laboratories, was used for facial prostheses but also was opaque and too rigid.

In 1916, the first translucent and low-modulus material for prosthetics was reported [2] as being used for artificial noses. This was a tinted mixture of gelatin and glycerol. The hygroscopicity of glycerol would cause fabricated parts to pick up moisture from the air or skin and lose their shape after a few days. Addition of potassium dichromate reduced the tendency for softening. Replacement of some of the glycerol by sorbitol [3] produced prosthetics which could last a few months (Clarke's "synthetic flesh").

Rubber latex, unvulcanized and vulcanized, often used for a mold-making material was also used in facial prostheses and was the best material for some applications until the vinyl resins became available. Rubber latex has problems with shrinkage, darkening with exposure to ultraviolet radiation, and the relatively slow fabrication procedure.

The workhorse materials for maxillofacial soft-tissue prostheses for the 25 years after World War II were the highly-plasticized vinyl resins, principally poly(vinyl chloride) and copolymers of vinyl acetate and vinyl chloride. These are generally used in the form of dispersed systems (colloidal sols) which gel irreversibly at elevated temperatures (typically 110-140°C). If the continuum is a nonvolatile plasticizer,

the system is known as plastisol; if volatile solvent is also present (usually to provide the conversion at a lower temperature), the system is called an organosol. By varying the ratio of plasticizer to resin the elastic modulus (stiffness) can be predetermined over a wide range.

For prosthetics applications, proprietary compositions (e.g., Mediplus, Flexiderm) have been available which have appropriate heat and UV stabilizers added, and in some cases are tinted to simulate skin tones. Final custom coloring is commonly accomplished by diffusion of oil-soluble dyes into the composition.

For some prosthetics applications, solutions of plasticized vinyl polymers (e.g., "Cordo Solution" [4,5]) are used. In such cases evaporation of the solvent is required during fabrication; thus multiple layers are needed to build up thick sections.

The advantages of the plasticized vinyl compositions include:

1. Low modulus (though with considerable loss of tensile strength when approaching the moduli of soft tissue structures),
2. Castability with replication of minute surface details from molds,
3. Good dimensional stability compared with earlier low-modulus materials,
4. Translucency which can be varied, and
5. Colorability after molding by dye diffusion.

Disadvantages of the vinyl plastisols and organosols include:

1. The requirement for high temperatures in the molding process—this prevents direct fabrication in agar and other moulage molds.
2. The high concentration of plasticizer in a gel structure leading sometimes to migration problems such as syneresis (formation of an oily surface film of plasticizer) or a solvent-type attack on surfaces such as lacquer finishes or polystyrene which the prosthesis might contact for a few hours,
3. Depletion of plasticizer from the outer layer of the prosthesis from volatilization or from washing with soap and water, leading to a stiffer surface than that present originally, and
4. Possible allergenic reactions from migration of plasticizers or from presence of necessary PVC stabilizers (absence of stabilizers can lead to HCl production).

Silicone elastomers of the polydimethylsiloxane type have been of interest because of their physiological inertness, their chemical stability, and their ability to be readily fabricated. Disadvantages of these

materials include low tear and tensile strength (particularly for very soft compositions) and lack of materials combining transparency and good physical properties.

A recent development by Southern Research Institute [6] has been with silphenylene polymers. These custom-synthesized silicone polymers provide very low modulus of elasticity, while maintaining good tear strength, ultimate tensile strength and elongation before break.

Another recent advance in materials for maxillofacial prostheses has been with certain urethane elastomeric compositions. One recently publicized system [7,8] is a three-part polyurethane system, Epithane-3 (Daro Products). By varying the ratio of the ingredients Shore A hardness from 5 to 50 can be obtained. The finished polymer has good transparency and reasonably long life (average reported to be nine months).

Our concept behind this project is that it should be possible to develop improved materials for maxillofacial prostheses within the context of *multiphase systems*, with our emphasis on the development and use of liquid-filled, elastomer-shelled microcapsules as ultrasoft fillers in prostheses. Specifically, we believe that it is possible to produce systems which can have the ultrasoft feel of some natural soft tissues (the hardest systems to duplicate), while retaining the required properties of strength and durability. Further, by the use of a new ultra-low modulus filler and a non-air-entraining, mixing-dispensing system to permit the prosthetist to work in a practical way with rapid-curing elastomers, we believe that effective systems fabricated entirely at room temperature can be developed.

1.2 Concepts for liquid-filled microcapsules in materials for prosthetics

External facial prosthetics, particularly where replication is of movable tissues, put hard demands on materials technology. Because the human soft tissues have complex mechanical properties which may vary from skin to underlying tissues and from place to place there is no single ideal material. Generally desirable properties for external maxillofacial prosthetic materials include:

1. Capability of being easily fabricated to various facial shapes and surface textures.
2. Ability to be colored internally and externally, with suitable translucency.
3. Mechanical properties (stress-strain behaviors) simulating those of skin and associated soft tissue.
4. Resistance to environmental factors, including sunlight, high and low temperatures, and humidity; retention of color and flexibility for extended periods of time.

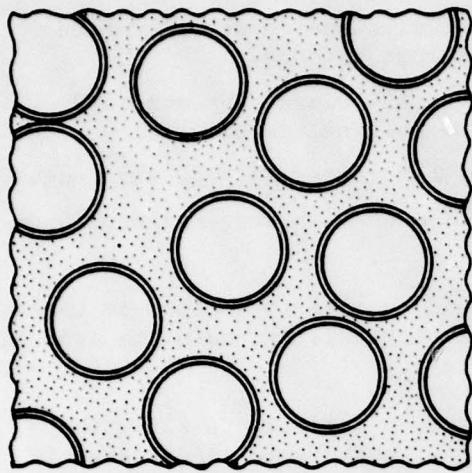
5. Nontoxicity to host tissues and resistance to deterioration associated with contact with the host tissues.
6. Capability, if soiled, of being easily cleaned by soap and water, without loss of surface or marginal details.
7. Resistance to tear and abrasion when molded to very thin edges.
8. Ability to be bonded to living tissues with surgical appliance cements or other skin adhesives.

The microcapsule-filled systems should be able to conform to these desirable characteristics. They would be particularly useful in item 3, matching the softness of the natural tissue.

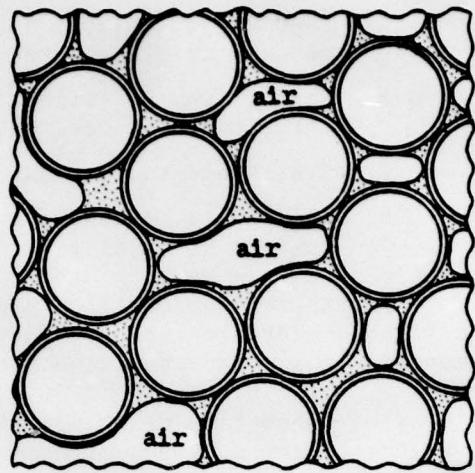
The concept of using the microcapsules as a filler to allow the varying of the softness of cast or molded structures is illustrated in Figure 1. Each of the configurations shown would provide structures of different softness. The elastomeric continuum with no capsules present (not illustrated) would have the highest elastic modulus. Configuration (a) would be somewhat softer. Configurations (b), (c), and (d) would represent ultrasoft structures, each probably having different shape of stress-strain curve. A recommended experimental study, once satisfactory liquid-filled, elastomeric-shelled microcapsules are obtained, is to determine how the mechanical properties of composite systems vary as a function volumetric fraction of microcapsules. From measured values in the literature for human soft tissues (For example, as reported by Yamada and Evans [9]) suitable compositions can be chosen for prosthetics fabrication.

How microcapsule composites might be incorporated into practical systems is a subject for future experimental study. Figure 2 illustrates schematically one possible configuration, showing how the system may be fabricated in layers. The choice of mold material can be more universal because of the room-temperature curing than is possible with PVC organosols and plastisols. Silicone rubber (with mold release if necessary), polysulfide rubber, waxed dental stone, and any of a number of hydrocolloids may be used for molds. The thin outer skin formed directly against the mold should be a very low modulus material, suitably translucent for coloring with dyes. Air curing silicone adhesives (e.g., GE RTV-118, DC 3144 RTV), low-modulus, color-stable polyurethanes, and the newer silphenylene elastomers are of interest here. As we have seen in our experience, an unpigmented ultra-sheer nylon mesh can provide reinforcement (preventing excessive elongations and tears), without detracting from the flesh-like feel. The mesh can be laid directly on the interface with the skin before curing occurs. Mass coloring techniques with fade-resistant dyes would be considered. Added localized coloring on the back surface of the skin can take place at this point.

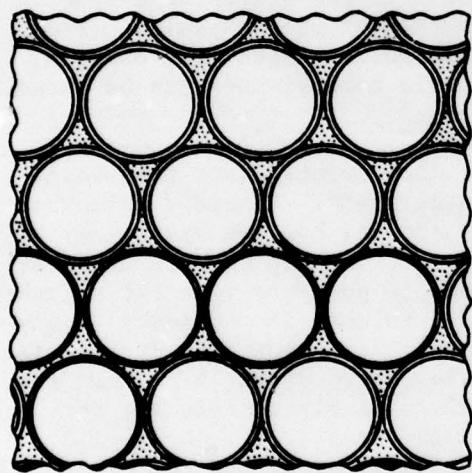
The next step is the addition of the thicker ultra-soft layer containing the microcapsules with room-temperature-curing binder. As noted earlier, by varying the ratio of capsules to binder — plus



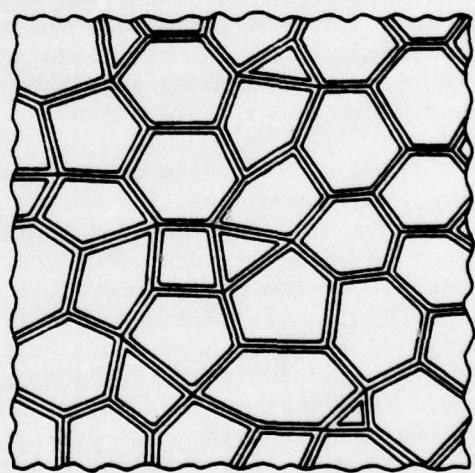
(a) Dispersion in an elastomeric continuum



(b) Loose packing bonded with elastomeric material, with some air spaces



(c) Close packing with elastomeric material in the interstices



(d) Compressed and bonded to form a cellular structure

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Figure 1. Schematic drawings of various ways in which liquid-filled elastomeric microcapsules might be used in composite structures for maxillo-facial prostheses.

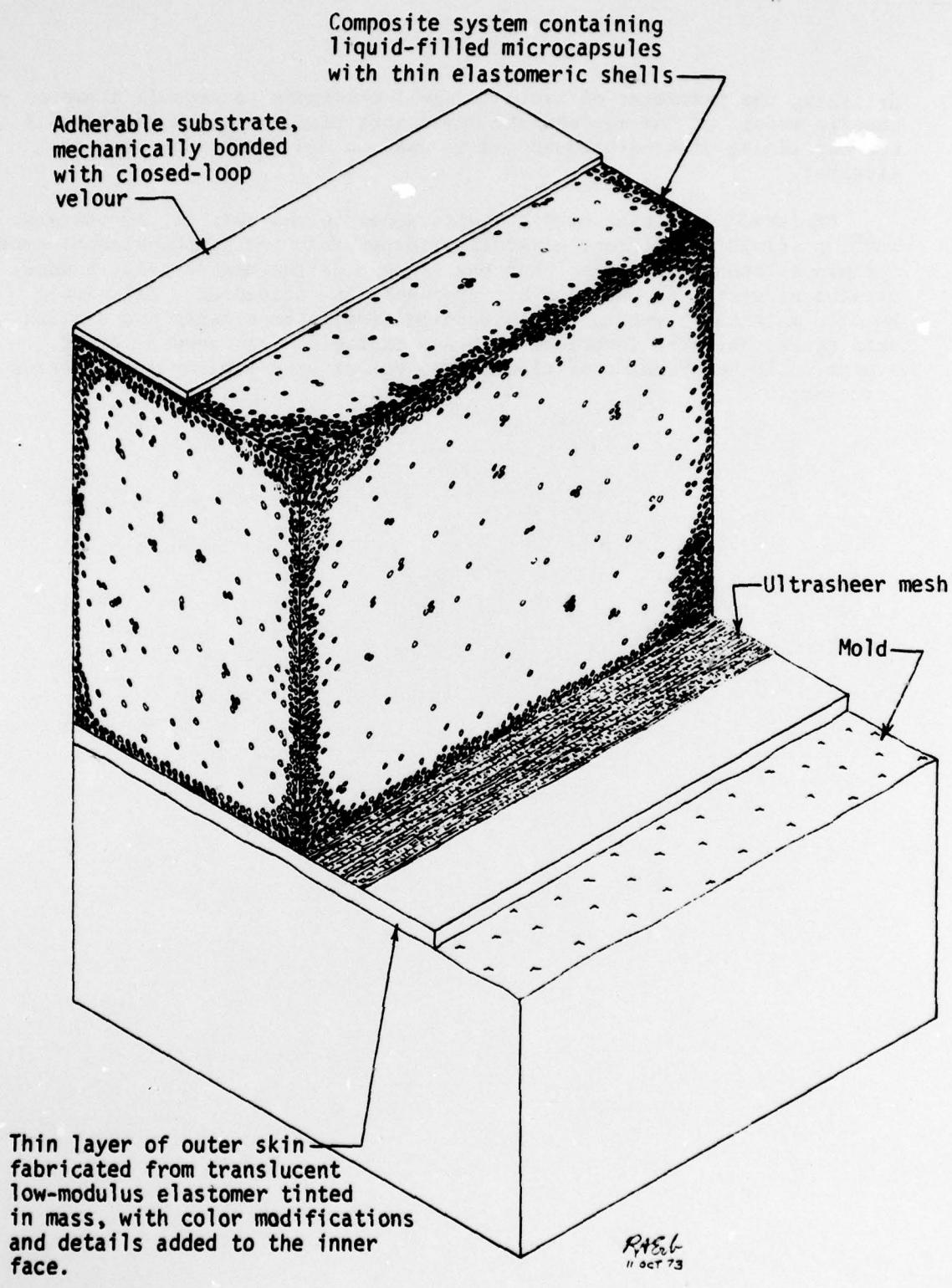


Figure 2. Schematic (enlarged) view of a prototype system for maxillofacial prostheses to be built up in layers from a mold

utilizing the parameter of ratio of shell thickness to capsule diameter — tensile moduli of the appropriate human soft tissues can be matched. A non-entraining mixer-dispenser can be used to mix the binder with its catalyst.

Finished prostheses need to be attached to the skin of the wearers. Nothing sticks to silicone elastomers (other than the silphenylenes) except certain silicone materials; thus the concept of the mechanically bonded attachment strip, as one possible approach, is introduced. This would be of a material compatible with surgical appliance cements and similar skin adhesives. The interlock with the castable microcapsule-filled system would be by means of closed-loop velour or a similar interlocking structure.

2. MICROENCAPSULATION STUDIES

2.1 Review of microencapsulation techniques

A basic question for this program relates to which one or more of the many microencapsulation processes show the most promise for producing elastomeric-shelled microcapsules containing an inert liquid. While much of the diverse field of microencapsulation is proprietary, there are several reference books [11, 12, 13], in addition to papers and patents.

General methods for microencapsulation include:

- (1) envelopment/coacervation (e.g., with gelatin walls);
- (2) emulsification/dehydration (or other solvent removal), including spray drying;
- (3) fluidized bed of core particles, spray coated;
- (4) fluidized bed of meltable coating material, with molten core droplets falling into it;
- (5) centrifugal forcing of core material through coating films;
- (6) electrostatic coating of aerosol droplets;
- (7) gaseous in situ polymerization (e.g., with p-xylylene) on the surface of solid (including frozen liquid) particles;
- (8) interfacial polymerization;
- (9) coaxial extrusion of core and shell material into a moving carrier-liquid stream.

Some of these methods are difficultly applicable to the encapsulation of liquids (particularly those with low freezing points) and some are not practical for use with suitable elastomeric materials for the shell. The last two approaches from this list, namely, coaxial extrusion and interfacial polymerization, are those which we believe have greatest promise for making elastomeric-shelled, liquid-filled microcapsules. The experimental effort in the first year's program has been directed toward developing these as practical procedures, using materials suitable for the microcapsules.

2.2 Core liquids

A study was made on what properties would be desirable for liquid core materials. The following list represents our present thinking as

to desirable properties of the liquids.

- (1) Low vapor pressure. This is so that a composite would not experience loss of mass and volume by volatilization.
- (2) Low freezing point. This is to avoid hardening of prostheses exposed to cold weather.
- (3) High molecular weight. This is to minimize diffusion through the elastomer of the shell.
- (4) Low potential for swelling or plasticizing the elastomer (or dissolving the elastomer precursor in coaxial extrusion), indicating that the solubility parameter of the core liquid and the elastomer should be significantly different.
- (5) Viscosity suitable for the particular capsule-forming process, and for the final product.
- (6) In interfacial polymerization, being, or being a solvent for, the reaction ingredient(s).
- (7) Chemical stability and inertness.
- (8) Low odor.
- (9) Low toxicity. In this regard some of the more interesting core liquids have extensive applications in cosmetics.

Table 1 lists some candidate core liquids. Samples of 13 of the listed materials were obtained for use in our experimental program.

2.3 Shell materials

The elastomers available for consideration for forming the microcapsule shells depend on the process to be used. For the coaxial extrusion process, a two-component curing type system seems most promising technically. Other approaches might involve the extrusion of a thermoplastic elastomer (with heating of the coaxial system, core liquid, and carrier fluid) or the extrusion of a single-component elastomer precursor such as the RTV silicone adhesive/sealants.

Two-component curing-type materials include silicones, polyurethanes and polysulfides. For use in prostheses the silicones and polyurethanes appear to be the materials of choice. A class of materials of basic interest is that of the polydimethylsiloxanes (with tetrapropoxysilane crosslinking agent) which can be rapidly converted from a viscous liquid to a rubbery solid by the addition of stannous octoate catalyst. Silastic 382 Medical Grade Elastomer and Silastic 399 Prosthetic Material (both Dow Corning products) are examples of the polydimethylsiloxane materials. Some of their properties are listed in Table 2. Silastic 382 is the material which we chose to use in most of our experimental studies to date relating to coaxial extrusion.

Table 1. Candidate Core Liquids for Elastomeric-Shelled Microcapsules

Material	Molecular Weight (or Avr. M.W.)	Specific Gravity 20/20°C	Boiling Point @ 760 mm Hg (°C)	Vapor Pressure at 20°C (mm Hg)	Freezing point (°C) ⁶	Solubility in Water % By Wt. @ 20°C	Viscosity
Propylene Glycol	76.1	1.0381	187.3	<0.1	-60 g1	complete	60.5 cps @ 20°C
Dipropylene Glycol	134.2	1.0232	232.8	<0.01	-40 pp	"	107 cps @ 20°C
Tripropylene Glycol	192.3	1.0193	272.9	"	-45 g1	"	"
Polypropylene Glycol 425	425	1.009	-	"	-50 g1	"	"
Polypropylene Glycol 1200	1200	1.004	-	"	-40 pp	2	160 cks @ 25°C
Polypropylene Glycol 2000	2000	1.003	-	"	-30 g1	0.2	230 cks @ 25°C
Polypropylene Glycol 4000	4000	1.002	-	"	-29 pp	0.1	114 cks @ 25°C
Polyethylene Glycol 200	200	1.1266	Decomp.	"	-65 g1	complete	4.1 cks @ 99°C
Polyethylene Glycol 300	300	1.125	"	"	-15 to -8	"	5.8 cks @ 99°C
Glycerol Triacetate	218.2	1.1604	258.0	"	-37 g1	5.8	"
Diethoxytetraglycol	250.3	0.9774	276.7	"	-21	complete	"
2-Ethyhexanol	130.2	0.8340	184.3	<0.1	-70 g1	0.07	"
Iso-Octanol (Mixed Isomers)	158.3	0.8406	220	<0.01	-60 g1	0.01	"
2,6,8-Trimethyl-1-4-Nonanol	186.3	0.8193	225.4	"	-60 g1	0.02	"
Hexylene Glycol	118.2	0.9233	197	<0.1	-50 g1	complete	35 cps @ 20°C
2-Ethy-1,3-Hexanediol	146.2	0.9422	243.2	<0.01	-40 g1	4.2	320 cps @ 20°C
1,5-Pentanediol	104.2	0.9921	242.4	"	-15.6	complete	128 cps @ 20°C
Polydimethylsiloxane 200	7000	0.971	-	"	-63	insoluble	200 cks @ 25°C
Polydimethylsiloxane 1000	11400	0.973	-	"	-58	"	1000 cks @ 25°C
Polydimethylsiloxane 10000	36000	0.973	-	"	-53	"	10000 cks @ 25°C
Ucon Fluid LB-65 ¹	-	0.963	-	"	-75 pp	"	"
Ucon Fluid LB-385 ¹	-	0.995	-	"	-35 pp	"	"
Ucon Fluid 50-HB-55 ¹	-	1.002	-	"	-85 pp	complete	"
Ucon Fluid 50-HB-400 ¹	-	1.046	-	"	-40 pp	"	"
Ucon Fluid 50-HB-660 ¹	-	1.052	-	"	-30 pp	"	"
UCC Silicone Fluid L-722 ²	-	0.99	-	"	-48	insoluble	125 cks @ 25°C
UCC Triol 3000 ³	3000	1.0098	-	"	-31	0.02	660 cps @ 20°C
Dow Polyglycol 15-200 ⁴	2600	1.063	-	"	-39 pp	complete	360 cks @ 25°C
Dow Polyglycol 112-25	-	1.023	-	"	-	-	-

¹Polyalkylene glycols and derivatives (UCC)
²Alcohol soluble; insoluble in dimethyl silicones
³Polyalkylene glycol adduct based on glycerine
⁴(H(OH₂C₃H₄C₂)₂CHO(C₂H₄OC₃H₆O)_nH
⁵A triol derived from ethylene and propylene oxides
⁶g1 = glass temperature; pp = pour point

Table 2. Properties of cured silicone elastomers

Property	Silastic 382 ¹	Silastic 399 ²	Silphenylene ³
Tensile strength, psi (ASTM D412)	400	525	1400
Elongation at break, % (ASTM D412)	160	230	1000
Tear strength, ppi (ASTM D624)	25	2	9
Modulus at 100%, psi	-	240	50
Hardness (Shore A)	43	50	35

¹Dow Corning Silastic 382 Medical-Grade Elastomer, cured with 5% Catalyst M (stannous octoate), after 24 hours at 25°C.

²Dow Corning Silastic 399 Prosthetic Material (discontinued)

³Silphenylene elastomer (Southern Research Institute)

Also listed in Table 2 is the newer silphenylene elastomer. (Silphenylene is short for polytetramethylsilphenylenesiloxanedimethylsiloxane.) This very interesting material, recently developed by Southern Research Institute [14], combines a low modulus of elasticity (very good for making ultrasoft composites) with high tensile strength and high elongation before break. Unfortunately it is not yet commercially available, but should nonetheless be an interesting material for future studies with microcapsule shells.

In addition to silicone systems, some urethane two-part casting materials may be of interest. Some of these have been used commercially in reaction injection molding (RIM), a rapid process carried out at elevated temperature for making large, usually high modulus elastomer. Problems with polyurethanes include: the need to provide a light color which doesn't darken on exposure to sunlight (requiring avoidance of the aromatic diisocyanate systems); the needed ability to have a rapid curing system at moderate temperatures; the inability to use aqueous neutral-density carriers because of interfering reactions; the need to produce soft materials in combination with low color and fast reaction rate. No experimental efforts with polyurethane systems for coaxial extrusion were undertaken in the first year program.

For the interfacial polymerization process a number of polymer classes have been suggested in the literature as wall materials. These include: polyamide (diacid chloride and diamine); polyester (diacid chloride and diol or polyol); polyurea (diisocyanate and diamine); and polyurethane (diisocyanate and diol or polyol). The bulk of the reported work is onpolyamide (nylon) walls. These are not elastomeric, however. The polyurethanes appear to be the class with the greatest potential for elastomeric wall formation, though some commercial polyester elastomers exist. We have not found in our literature searches any reports of microcapsule formation by interfacial polymerization with urethane elastomer walls. The emphasis in our experimental program with interfacial polymerization to date has been with the polyurethane systems.

2.4 Experimental studies with coaxial extrusion

Figure 3 represents a conception of the coaxial extrusion process which we had before the start of the program. The extrudate would be suspended in a neutral-density liquid flowing in the direction of the extrusion at the same velocity as the extrudate, or, in accordance with the method of G. R. Somerville of Southwest Research Institute, at a higher velocity than the extrudate. The well-known instability of a cylindrical liquid stream which causes formation of discrete drops indeed does work very well with water, molten waxes, and similar low-viscosity liquids. However, the elastomer precursors may be 10,000 times the viscosity of water (100 poises versus 1 centipoise), and the processes of necking down and droplet formation do not occur in the time available before wall impacting or getting of the extruded stream. Thus we have found that we need a "chopping" mechanism of some sort.

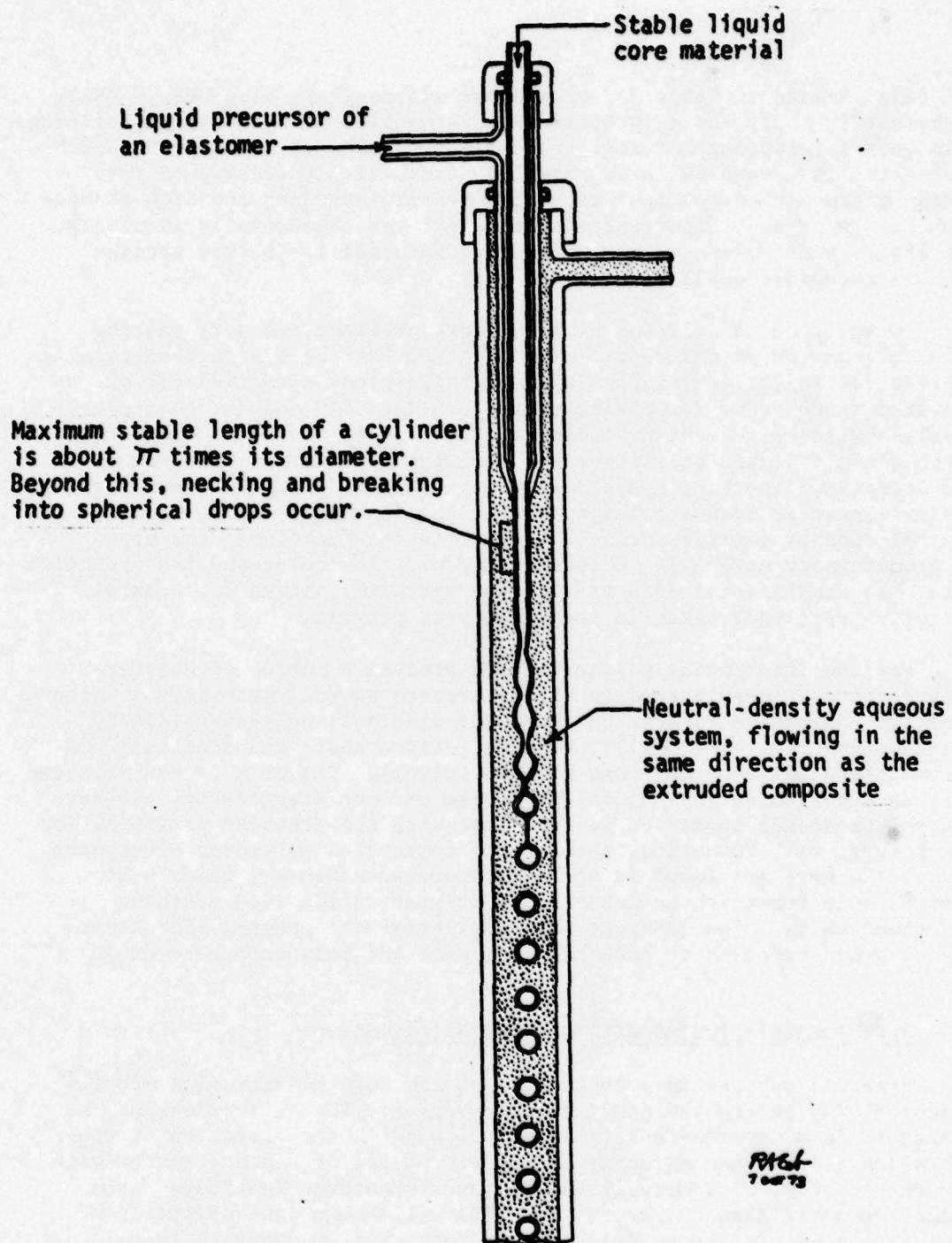


Figure 3. Technique for producing microcapsules to be used as modulus-lowering fillers in maxillofacial prostheses

Our earliest experiment which showed that necking and droplet formation does not occur with high viscosity systems was with a stream of RTV 118 (General Electric), a flowable moisture-curing system with about 890 poise viscosity.

In the next stage of experimental development we used the apparatus shown in Figure 4 for extruding a stream of two-component elastomer precursor into an aqueous bath. A variable-speed, torque-independent drive provided a preset displacement rate for the pistons of a syringe with a silicone elastomer precursor and a syringe with stannous octoate catalyst. By varying the ratio of the piston areas a predetermined volumetric ratio of elastomer precursor and catalyst (e.g., 60 to 1) could be maintained. By increasing or decreasing the catalyst concentration the gelling time can be varied from about a minute after mixing to more than 10 minutes. The temperature of the receiving bath will also affect the gelling and curing rate; the bath is warmed if a faster cure is desired.

A critical component in the system is the inline mixer. This element divides and twists repeatedly the combined streams of elastomer precursor and catalyst so as to provide thorough mixing. Commercial examples of these exist, such as Kenics "Static Mixer" (bow-tie twisted metal elements) or Devcon "Auto-Mix" (injection molded plastic element). For our studies, we have used stainless steel curled flattened wire packed into glass or later metal tubes about 5 cm in length. This packing material is available as stainless steel cleansing pads (e.g., Gottschalk Pot Cleaners). Initially it was difficult to determine how long the mixing element needed to be to accomplish thorough mixing of the catalyst and elastomer precursor. This problem was solved by lightly coloring the stannous octoate with a rhodamine red dye. Coloring of the entire mass of initially white silicone material indicates that the catalyst is well mixed in.

Figure 4 and Figure 5 show the use of a rotating bath to carry an extruded stream. The catalyzed material being extruded in these photographs is Silastic 382 Medical Grade Elastomer. It is denser than the water (1.13 g/cm^3 vs 1.00 g/cm^3) and thus sinks to the bottom. The material also spirals into the center, reflecting perhaps a Coreolis effect. In the illustrated case, a solid object was formed resembling a Hershey candy kiss.

Figure 6 shows schematically one system for coaxial extrusion to produce microcapsules with catalyst-cured shells. (Figures 7 and 8 relate to interfacial polymerization and will be discussed later.) The experimental studies, starting with the schematic concept, showed that the procedure is not easy. Particular problems which we attacked were: (1) high back pressure in the feed system from viscous flow of elastomer precursor through the annulus in the extrusion head; (2) difficulties in chopping to form closed-wall capsules of reasonably small sizes; (3) tendency of formed capsules to agglomerate before curing, when

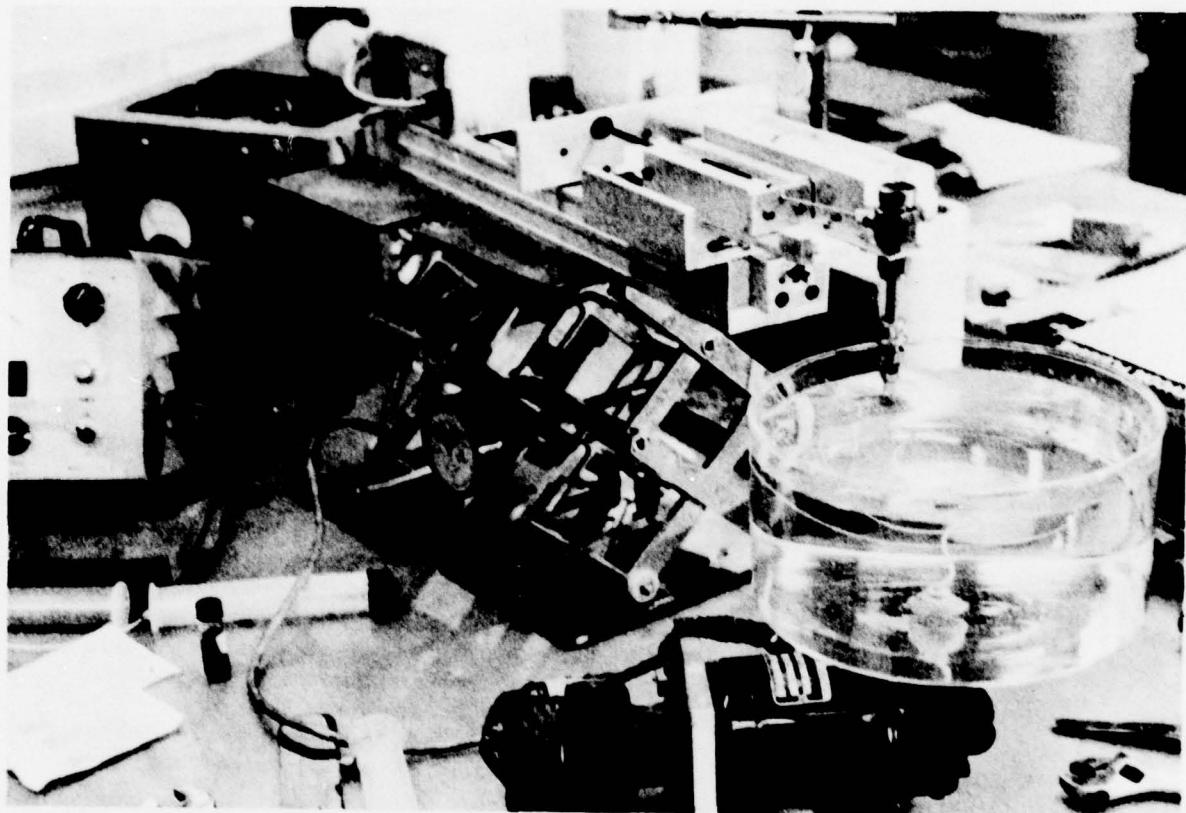


Figure 4. Experimental apparatus for coaxial extrusion, arranged for simple extrusion of Silastic 382 and stannous octoate catalyst, with an in line mixer; variable speed piston drive and rotating bath are shown.

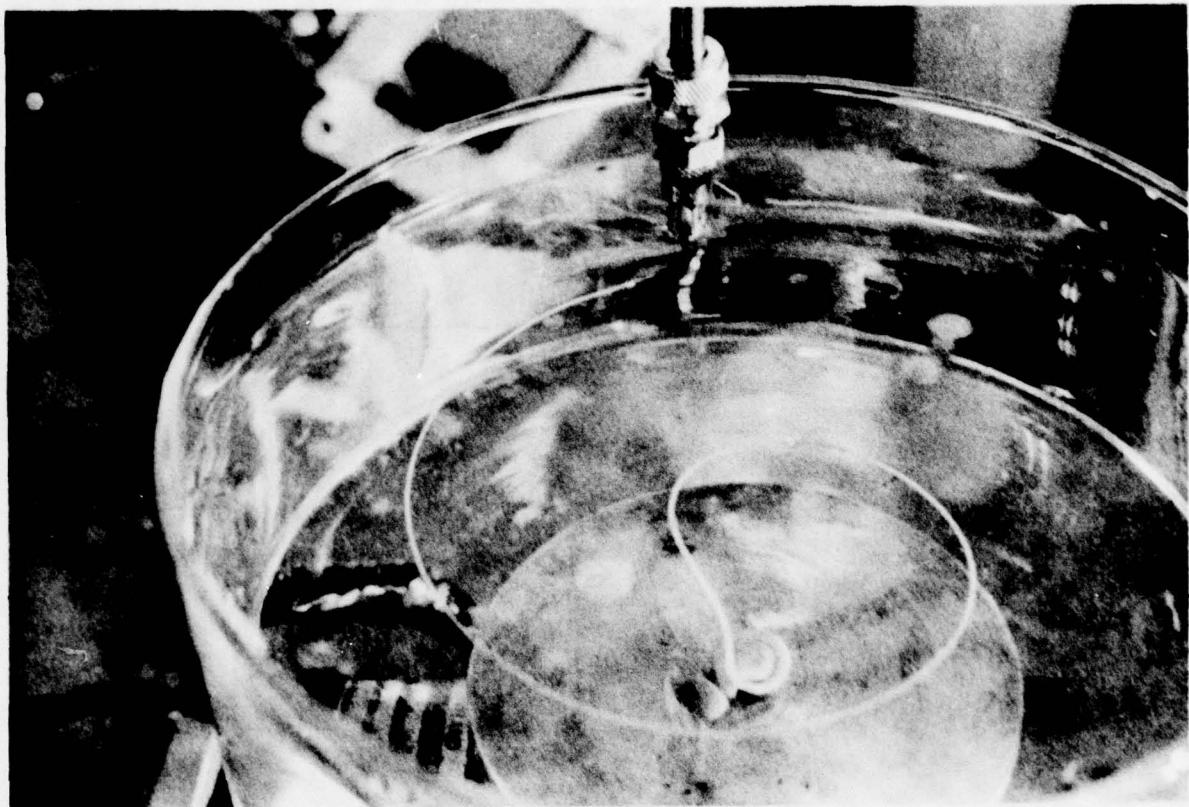


Figure 5. Behavior of an extruded elastomer-precursor filament in a rotating uniform-density bath.

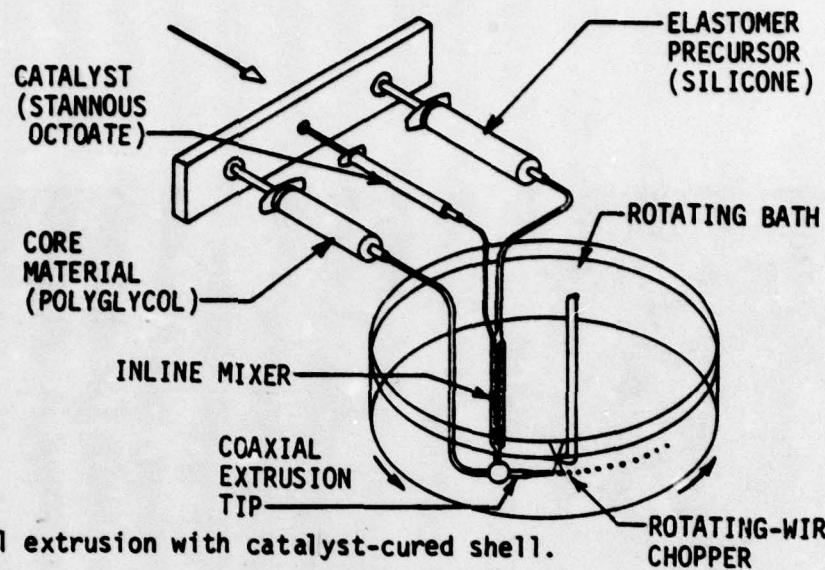


Figure 6. Coaxial extrusion with catalyst-cured shell.

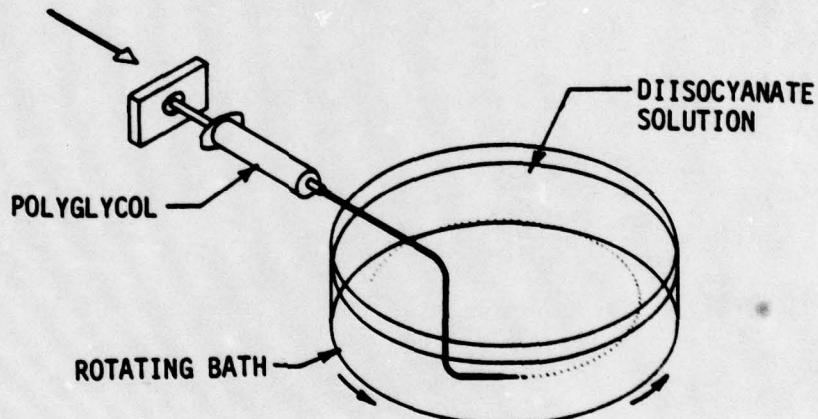


Figure 7. Extruded uniform-size droplet formation for interfacial polymerization.

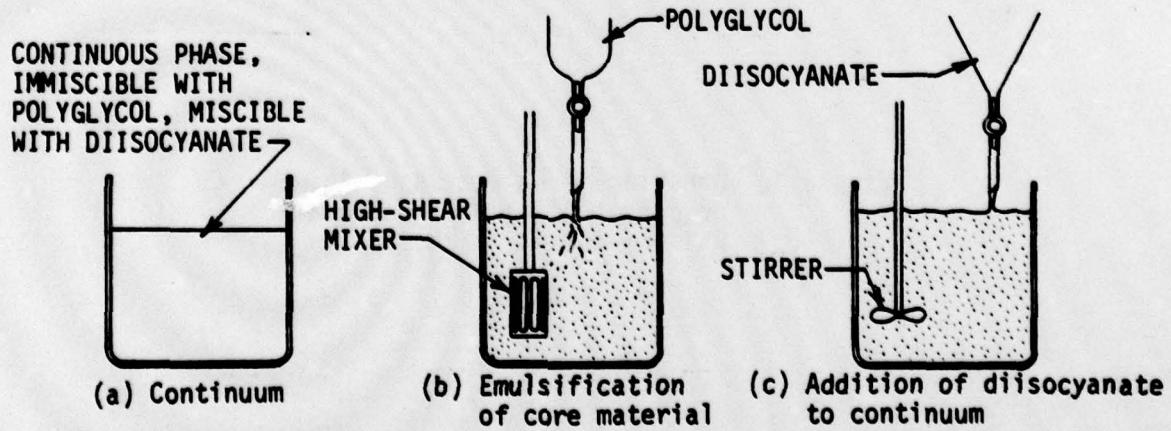


Figure 8. Emulsification, followed by interfacial polymerization.

contacting the floor of the vessel and uncured material in the bath; (4) quality control problems, particularly how to determine which capsules are liquid filled and have intact walls.

Our initial extrusion studies were with Silastic 382 Medical Grade Elastomer. This has a viscosity of about 500 poises. The first experiments used a 50 cm³ syringe with a polypropylene barrel. With the high viscosity material the internal pressure caused leakage around the piston by swelling of the barrel. By the addition of 20 parts by weight of 20 centistoke silicone fluid to 80 parts of Silastic 382, a viscosity of about 100 poises was obtained. Further improvements made were fabrication of an o-ring-sealed piston and a metal support sleeve to prevent barrel swell.

Flow expressions for a Newtonian material and circular annular ducts (derived from expressions in : Martin H. Wohl, "Dynamics of flow between parallel plates and in noncircular ducts," Chemical Engineering, 6 May 1968, pp. 183-186) are as follows:

Design equation:

$$Q = \frac{\pi (r_o + r_i)(r_o - r_i)^3 \Delta P}{12nL} \quad (1)$$

Shear stress at the walls:

$$\tau_w = \frac{(r_o - r_i) \Delta P}{2L} \quad (2)$$

Shear rate at the walls:

$$\left(\frac{dy}{dt}\right)_w = \frac{6Q}{\pi (r_o + r_i)(r_o - r_i)^2} \quad (3)$$

where: Q is the volumetric flow; r_o and r_i are the outer and inner radii of the annulus; ΔP is the pressure drop along the length of the annulus; n is the Newtonian viscosity of the liquid elastomer precursor being extruded; L is the length of the annulus; τ_w is the shear stress at the walls; and (dy/dt)_w is the rate of shear at the walls.

Using concentric hypodermic tubing as the model for coaxial extrusion, with a 13-gauge outer tube and 16-gauge inner tube combination (r_o = .08255 cm and r_i = .09017 cm), a viscosity of 100 poises, an annular length of 0.8 cm, and a flow of elastomer precursor of 50 cm³/hour, the calculated back pressure is 806 psi. Even at such a low flow rate the piston force is higher than the desired limit for the variable speed

drive used in the experimental program to date. Indeed the threads of the nylon drive nut were stripped in one run.

We propose to construct a high-pressure system with capabilities to perhaps 4000 psi. A hydraulic-actuated force system will operate simultaneously on two pistons, one for flow actuation of the elastomer precursor and the other for flow actuation of the catalyst. The core liquid will continue to be fed with a separate controlled-variable-speed motor drive. This separate driving of core liquid has already been shown in our experiments to be useful; this is distinguished from the arrangement shown in Figure 6 in which one pusher acts on three pistons.

One of the most difficult problems (one still unsolved) has been in chopping the coaxial stream so as to form capsules with intact elastomer walls, and also producing capsules in a desirable size (smaller than 2mm in diameter).

Attempting to produce cutoff by extruding into a faster moving stream does not work by itself. With a given shell material, necking down occurs more readily with lower-viscosity core liquids; for example, polypropylene glycol 425 gives much better stream breakup than polypropylene glycol 4000, which is more than ten times as viscous. While some breaking of the stream into units occurs with the simple use of a moving carrier liquid this breaking occurs at relatively long intervals and large pieces of material are formed, usually with a ruptured wall allowing loss of the core liquid.

Mechanical methods tried in this program for cutoff of the coaxially extruded stream include:

- (1) hand vibration of a microspatula across the stream; this method is useful because it allows quick feedback in controlling frequency and amplitude of the vibrations to get the best breakup with the method;
- (2) propellor-type mixer blade driven with an electric motor; this is the poorest of the techniques studied, as the produced turbulence destroyed the streamline flow of the bath relative to the extrusion head and also whipped-in air bubbles.
- (3) rotating head with several thin wires protruding, powered by a variable speed dental drill system; this was better than the propellor system but also introduced turbulences and the wires quickly became fouled with the sticky silicone material.
- (4) vibrating wire or needle mounted in an electric toothbrush; this vibrating system gives less turbulence than the rotating systems but also gets fouled.

(5) vibrating blade with high amplitude, actuated by a saber saw drive; this was superior to rotating blades but did not give the control that the manual spatula movement did.

Two problems with all of the above cutoff approaches are: (1) that they do not positively pinch the walls together before the stream is broken up, and (2) that the viscous silicone liquid sticks to the cutoff members, interfering with their function. In the underwater situation the silicone has been seen to stick more readily to hydrophobic than to hydrophilic surfaces. As a practical matter we have seen it stick to any of the various cutoff tools at some point during an extrusion procedure. Once this happens, the cutoff function is adversely affected, and repeated wiping off is needed.

One thing that the silicone won't "stick to" is water (and aqueous solutions). Thus we are proposing for the program continuation to use controlled pulsed jets of high pressure aqueous solution in the cutoff process. Two opposing jets, with synchronized pulses, will be studied experimentally toward getting a clean pinching off of sealed microcapsules. Parameters include: peak velocity of the jet; pulse shape and frequency; shape of nozzles (circular, fan shaped, etc.); distance of the jet orifice from the coaxial stream; angle of the jet with respect to the stream (90°, or angled toward the direction of the extrusion); and distance of jets from the coaxial extrusion die. (Three or more jets may also be found to be useful.) It is possible that something as simple as the commercial pulsed jets for dental hygiene (Water-Pik, Aquajet, etc.) may be suitable for cutoff. However, the need for a controlled frequency and higher jet pressures may require assembly of a specially designed system.

The tendency for formed capsules to agglomerate before curing, when contacting the floor of the vessel and other uncured material in the bath was overcome experimentally in this program. The particularly successful approach used to avoid this problem has been the use of a graded-density bath. This is readily formed, starting with a sodium chloride solution with a predetermined uniform density such that liquid filled microcapsules would just sink. A suitable concentration gradient is achieved by adding solid salt to the bottom and allowing the bath to stand for a few hours. A carefully laid-in top layer of pure water prevents flotation of materials (e.g., some capsules with an attached air bubble) to the surface. Agglomeration of formed capsules is effectively prevented because the spheres are not all in the same plane and rarely touch. The high-density lower layer of liquid positively prevents the formed spheres from touching the bottom of the vessel. A larger vessel than that shown in Figures 4 and 5 was introduced and has also helped in preventing agglomeration; this larger vessel is 12 inches in diameter by 18 inches high.

Figure 9 shows agglomerated silicone rubber (Silastic 382) capsules with polyethylene glycol 200 core liquid. These were formed by coaxial extrusion in a rotating bath with uniform-density sodium chloride

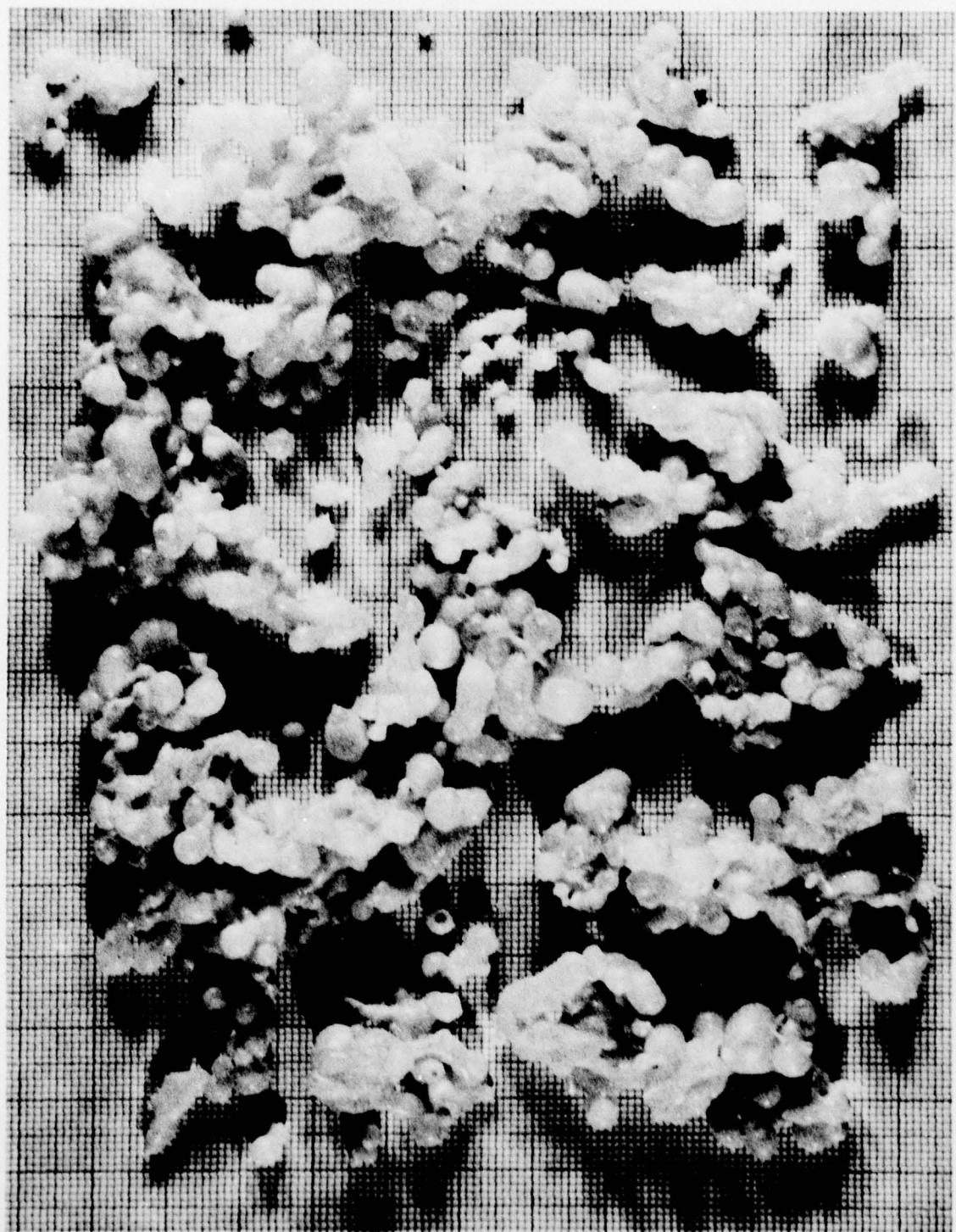


Figure 9. Agglomerated capsules, mostly ruptured, formed by coaxial extrusion of Silastic 382 shell and polyethylene glycol 200 core in a rotating, uniform-density salt solution.

solution. Without a density gradient, agglomeration occurred on the vessel floor.

Figure 10 shows the difference in product shape with the use of a density-gradient bath. The product consists principally of individual spheres. Many of the spheres shown are solid and do not contain the polyethylene glycol 200 liquid core material. That is, the rupturing with manual chopping would often release the core contents, leaving only the shell material which then assumed the spherical shape before curing.

The quality control problem is an important one, particularly in defining which spherical particles have liquid cores, and, further, what ratio of liquid to solid exists. Cutting the capsules open, of course, is destructive and not generally useful. A step toward solving this was made experimentally in substituting polypropylene glycol 425 (density 1.009 g/cm³) for polyethylene glycol 200 (density 1.127 g/cm³). The latter density is very close to that of Silastic 382 (density 1.13 g/cm³), which is lowered somewhat (to about 1.10 g/cm³) by the addition of the viscosity-reducing silicone diluent (density 0.97 g/cm³). The low density of the polypropylene glycol 425 allows for flotation separation of good capsules (containing suitable fractional volumes of core liquid) and unsatisfactory capsules (in which the fraction of core liquid is too low or nonexistent). In a graded density bath with floating density standards, capsules with particular core/shell ratios can be identified and recovered. Recovery of capsules from the bath can be made with a long-handled screen or with an aspirator.

Figure 11 is a drawing of a liquid-filled microcapsule made by coaxial extrusion of viscosity-modified Silastic 382 with polypropylene glycol 425, with flotation separation. The drawing was made from a stereoscopic microscope examination of a sphere sliced in half with a razor blade. The sphere was seen to be multicompartimented, rather than a single cell microcapsule. This may develop from the manual chopping procedure, wherein smaller capsules were formed and pushed together into the large mass. The larger mass would form by surface free-energy considerations the essentially spherical shape seen. While the multi-compartmented capsules have the significantly softer feel sought (as compared with solid rubber spheres), single-celled, sealed microcapsules are the goal which will be sought in the continuing program.

2.5 Experimental studies with interfacial polymerization

Interfacial polymerization has several attractive features as a potential method for making elastomeric-shelled microcapsules:

- (1) very thin-walled capsules should be possible (much thinner than may be practical with coaxial extrusion); thus favoring an ultrasoft product.

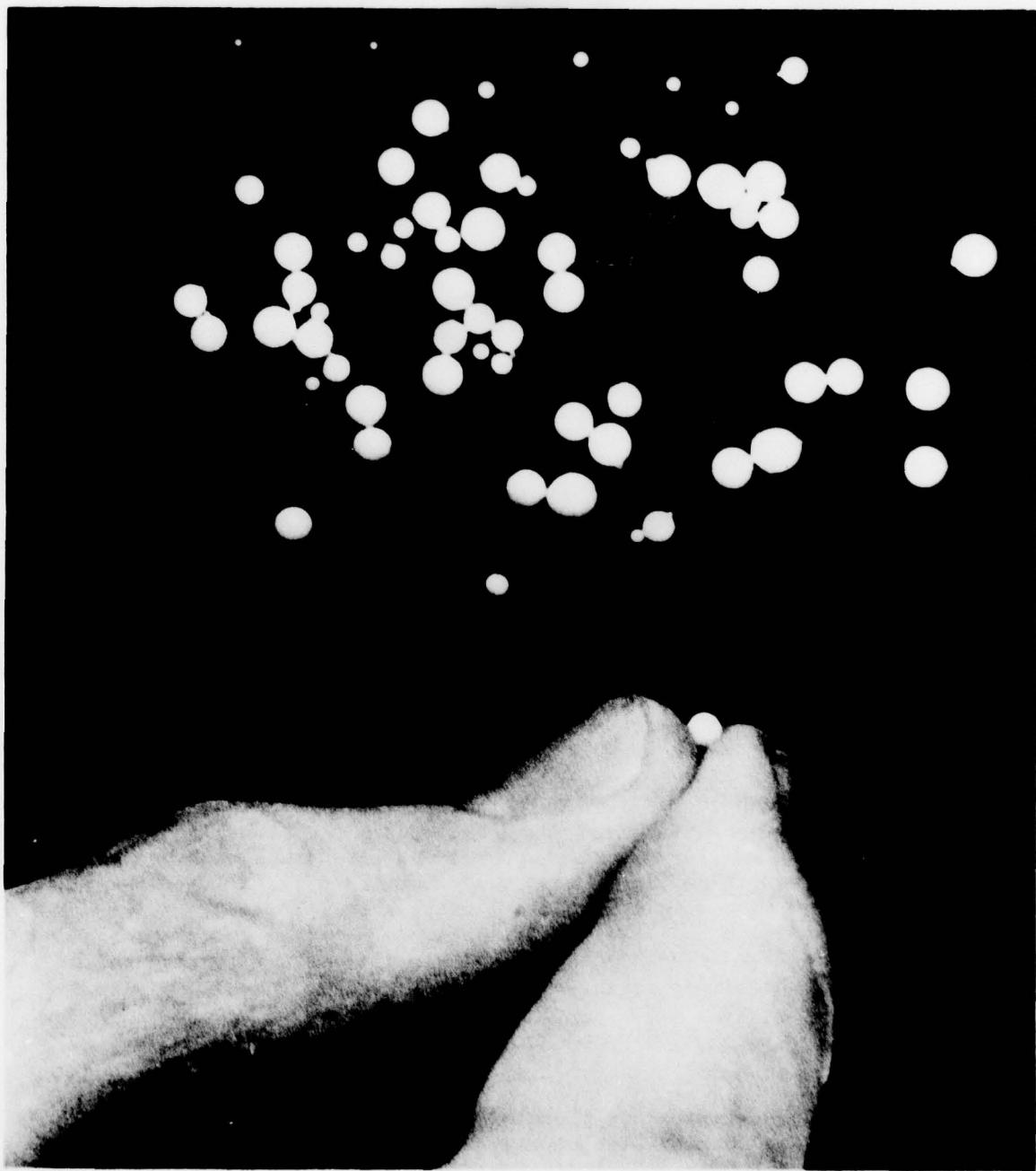


Figure 10. Silastic 382 spheres formed by coaxial extrusion with polyethylene glycol 200 core liquid into a stationary, density-gradient bath.

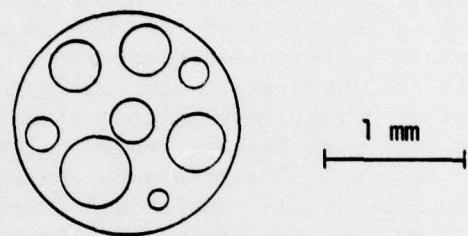


Figure 11. Sectional view of a spherical silicone rubber capsule with multiple cavities filled with polypropylene glycol 425; a product of coaxial extrusion with hand chopping.

- (2) capsules with very small outside diameters should be possible;
- (3) the interfacial reactions of greatest interest, polyol-diisocyanate reactions to form polyurethane elastomer, may utilize some of the core liquids of interest (listed earlier in Table 1) as both core liquids and polyol reactants.

Figures 7 and 8 (noted briefly earlier) are schematic illustrations of two general methods of making microcapsules by interfacial polymerization, involving a first step of droplet formation. Figure 7 shows formation of individual droplets of the core liquid in an immiscible continuum containing reactive diisocyanate material. The size of droplets formed are related to the diameter of the tubing through which the core liquid flows. In the principal experimental effort to date, a vertical long tube has been used with falling drops instead of the rotating bath illustrated. Figure 8 illustrates an emulsion process for microcapsule formation. Because of the greater difficulty in controlling drop size and size distribution, this method has presently been set aside in favor of the extruded stream approach.

Appendix A, by S. W. Osborn and R. A. Henning, describes the initial experimental development efforts with the interfacial polymerization process.

In the proposed continuation effort, we plan to attack the various problems which have been encountered. The need for a faster curing rate is evident. Approaches to be considered include: study of various combinations of diisocyanates with diols/triols; study of various catalyst combinations; use of heat to accelerate the curing reaction; and use of UV-initiated curing reactions. To prevent sticking and clumping at the bottom of the tube, approaches to slowing the falling rate of droplets will be considered including: increasing the viscosity of the external phase (e.g., by use of a polymer solution); increasing the density of the external phase (by choice of denser solvents than kerosene); and decreasing the droplet size by use of smaller tips (various sizes of hypodermic needles). To prevent or reduce contact of the spherical particles with each other or with the vessel walls and bottom we propose to consider: use of a much wider collection vessel at the bottom of the falling tube; and use of a density gradient in the collection vessel so that formed microcapsules remain suspended until collected. Preventing cure-through will involve choosing combinations of polyol and diisocyanate in which the diisocyanate is not significantly soluble in the polyol, and also the study of inert core liquid bases in which the polyol is soluble but not the diisocyanate. Possible candidates include inert polyethers and alcohol-soluble silicones.

REFERENCES

- [1] Clarke, Carl Dame. *Prosthetics*. The Standard Arts Press, Butler, Maryland, 1965.
- [2] Zinsser, F. *Zur Technik der anfertigung kunstlicher Nasen*. Munchen med. Wehnschr. 63, pp. 511-513, 1916.
- [3] Clarke, Carl Dame. *New Improvements in Moulage Prostheses*. J. Lab. and Clin. Med., 28, pp. 1399-1414, 1943.
- [4] Gearhart, Donald F. *The Compounding of 'Cordo Solution' for Prosthetic Applications*. Bull. Pros. Res., BPR 10-16, pp. 130-148, 1971.
- [5] Gearhart, Donald F. *Polyvinyl Chloride (Cordo) Facial and Body Prostheses*. Bull. Pros. Res., BPR 10-13, pp. 214-218, 1970.
- [6] Lewis, Danny H., Miller, David P., and Conway, Donald R., "Development of Improved Materials for Extraoral Maxillofacial Prostheses," 2nd Annual Report, PB-258002, NTIS (June 1976).
- [7] Anon., "Plastics Mask Scars of Surgery," Chemical Week, p. 42, 15 December 1976.
- [8] Anon., "Lifelike Prostheses of Urethane Repair Damage of Facial Surgery," Modern Plastics 54, No. 3, pp. 30,32 (1977).
- [9] Goodwin, John T., and George R. Somerville. *Physical Methods for Preparing Microcapsules*. Preprint Volume 33, No. 2, Division of Organic Coatings and Plastics Chemistry, American Chemical Society, pp. 611-617, 1973.
- [10] Yamada, Hiroshi (F. Gaynor Evans, Ed.). *Strength of Biological Materials*. The Williams and Wilkins Company, Baltimore, Maryland, 297 pages, 1970.
- [11] Nixon, J. R., Ed. *Microencapsulation*. Marcel Dekker, Inc., New York, New York, 215 pages, 1976.
- [12] Vandegaer, Jan E., Ed. *Microencapsulation Processes and Applications*. Plenum Press, New York, New York, 180 pages, 1974; Proceedings of the American Chemical Society Symposium on Microencapsulation: Processes and Applications, Chicago, 28 August 1973.
- [13] Gutchko, M. H., *Microcapsules and Microencapsulation Techniques*. Noyes Data Corporation, Park Ridge, New Jersey, 351 pages, 1976.

REFERENCES (cont.)

[14] Lewis, Danny H., Miller, David R., and Cowsar, Donald R., *Development of Improved Materials for Extraoral Maxillofacial Prostheses*. NTIS, Report No. PB 258 002, June 1976.

GENERAL REFERENCES

Bulbulian, Arthur H. *Facial Prosthetics*. Charles C. Thomas, Springfield, Illinois, 416 pages, 1973.

Rahn, Arthur O. and Boucher, Louis J., *Maxillofacial Prosthetics: Principles and Concepts*. W. B. Saunders, Philadelphia, Pennsylvania, 1970.

Robinson, John E., and Victor J. Niiranen (eds). *Maxillofacial Prosthetics, Proceedings of an Interprofessional Conference, September 1966*. U.S. Govt. Printing Office, 269 pages, 1969.

S. W. Osborn
R. A. Henning

Development Study — Glycol Filled Polyurethane Spheres

The efforts toward preparation of liquid-filled spheres encapsulated in a flexible polyurethane skin using an interfacial technique have continued.

In the process under study, glycol droplets were allowed to fall by gravity through a column containing one or more diisocyanates in an inert, immiscible solvent. The isocyanate phase contains a small amount of an organotin catalyst (stannous octoate).

Experiments Using TDI

In experiments using toluene diisocyanates (TDI)/kerosene as the external phase, polymeric skins were obtained with TDI conc. >35% at 50°C, with 0.5% stannous octoate, using a polyglycol mixture consisting of low molecular weight diols and triols with an average segment length of 200-400 molecular weight units.

The products were hard and brittle, and unsuitable for the purpose intended.

The use of higher molecular weight polypropylene glycols (Dow Polyglycol P2000 and P4000) gave a slower reaction at room temperature. At elevated temperature, solubility of the higher glycols resulted in premature rupture of the urethane skin, and subsequent through-cure of the urethane shell.

Experiments Using Aliphatic Diisocyanates

Three types of aliphatic diisocyanates are under investigation. They are:

- a. Hexamethylenebis(isocyanate) (Mondur HX-Mobay)
- b. Isophorone diisocyanate (Veba-Chemie A.G.)
- c. Methylenebis-(4-cyclohexyl isocyanate) (Hylene W, Du Pont)

Of the aliphatic diisocyanates, Mondur HX (aliphatic NCO) normally reacts most quickly to form urethanes, followed by isophorone diisocyanate. The latter contains one aliphatic and one slower reacting alicyclic isocyanate. Hylene W (two alicyclic isocyanates) reacts most sluggishly.

At room temperature, using isocyanate concentrations up to 40% in kerosene, beads with sufficient skin structure to permit isolation could not be obtained.

High Viscosity Urethane Bead Polymerization

A promising modification of the present system lies in the use of a high viscosity mineral oil as external solvent for the diisocyanate. Using a 4 ft. long vertical reaction tube, droplet falling time was increased from 3 - 10 seconds to 90 - 120 seconds and longer reaction times are possible.

Experiments are continuing with this system using Polyglycol P2000 and/or P4000, together with a triol (Dow Polyglycol 112-2) at elevated temperatures. The cured urethane product from this system exhibits a suitably low modulus of elasticity, however reaction rates are still too slow to give glycol-filled beads of the type desired.

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